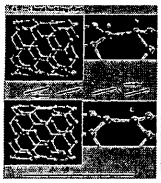
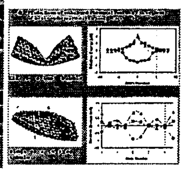
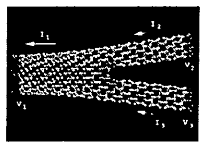
Mechanics of Nanotubes and Nanotube-Polymer Composites

Deepak Srivastava, NASA Ames Research Center
Chengyu Wei, Stanford University/NASA Ames
Kyeongjae Cho, Stanford University
Madhu Menon, University of Kentucky
Mohamed Osman, Washington State University/Pullman

NASA Mission Needs

- Onboard computing systems for future autonomous intelligent vehicles
  - powerful, compact, low power consumption, radiation hard

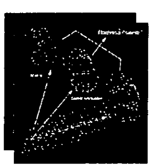
- High performance computing (Tera- and Peta-flops)
  - processing satellite data
  - integrated space vehicle engineering
  - climate modeling
- Revolutionary computing technologies
- Smart, compact sensors, ultrasmall probes
- Advanced miniaturization of all systems
- Microspacecraft
- 'Thinking' spacecraft
- Micro-, nano-rovers for planetary exploration

Carbon Nanotube

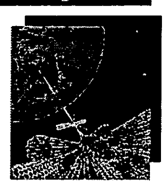
Ames Research Center

CNT is a tubular form of carbon with diameter as small as 1 nm. Length: few nm to microns.

CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.



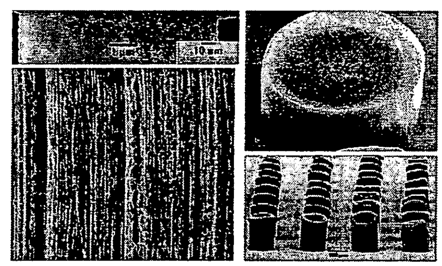
CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.



CNT can be metallic or semiconducting, depending on chirality.

Experimental Nanotechnology at Ames Research Center

CVD Carbon Nanotube SEM Images



http://www.ipt.arc.nasa.gov at Ames Research Center

Outline

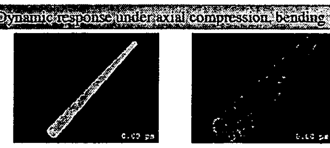
- Nanomechanics of nanotubes (C and BN nanotubes)
  - plastic collapse
  - anisotropic strain-release
  - nanostructured skin-effect
- C nanotube reinforced polymer composite
  - increased thermal expansion coefficient
  - increased Young's modulus
  - mechanisms and limits of load transfer

Nanomechanics of Individual Nanotubes

Nanotubes are extremely strong highly elastic nanofibers

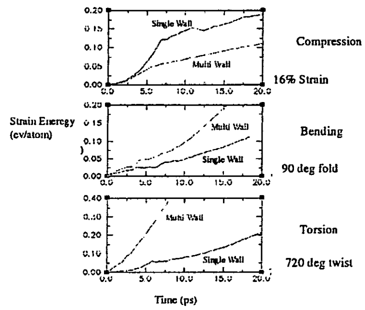
- **High value of Young's Modulus (1.2 -1.3 T Pa for SWNTs)**
- **Elastic limit upto 10-15% strain**

Dynamic response under axial compression, bending torsion



- *redistribution of strain*
- *sharp buckling leading to bond rupture*
- *SWNT is stiffer than MWNT*

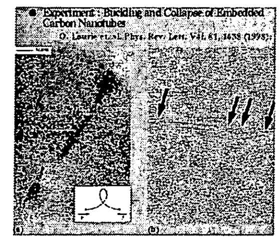
Nanomechanics of Individual Nanotubes



Nanotubes in Composites

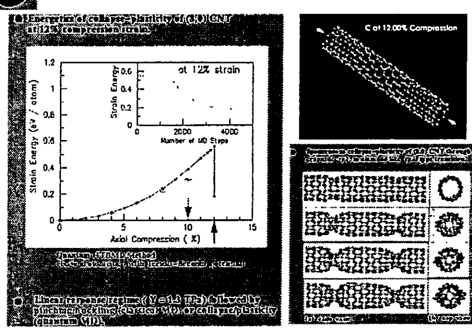
• Experiment: buckling and collapse of nanotubes embedded in polymer composites.

Buckle, bend and loops of thick tubes..



Local collapse or fracture of thin tubes.

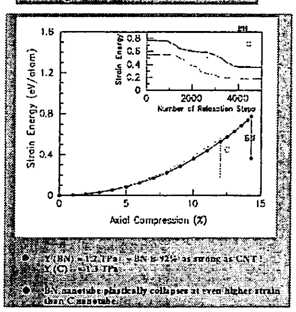
Stiffness and Plasticity of SW C Nanotubes



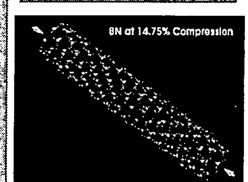
D. Srivastava, M. Menon and K. Cho, Phys. Rev. Lett. Vol. 83, 2973 (1999)

BN Nanotubes: Nanomechanics and Plasticity

• Young's modulus and elastic limit



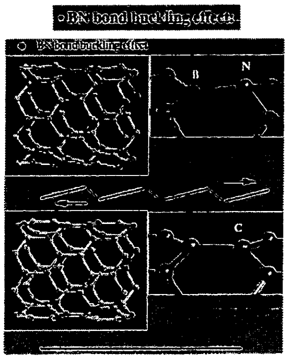
• Anisotropic strain release and plastic collapse



D. Srivastava, M. Menon and K. Cho, Phys. Rev. B. to appear, 2001

BN Nanotubes - Structural Characteristics

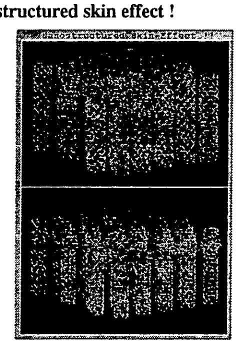
• BN bond buckling effects



BN Nanotubes - Nanomechanics

• BN nanotube based composite with anisotropic plasticity

• **Nanostructured skin effect !**



Yielding Strain of CNT

Tension

Simulation: 30% yielding strain from fast strain rate (1/ps) molecular dynamics simulations

Experiments: 6% maximum strain in SWCNT ropes; 12% maximum strain in MWCNTs

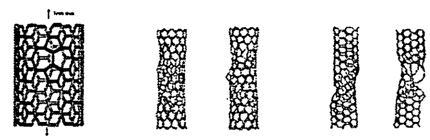
Compression

Simulation:
T=0K, Tersoff-Brenner potential: Super-elastic up to 20%
T=0K, Tight Binding: diamond like defects, collapsed at 12%

Experiment:
Collapsing of CNT within polymer matrix under compression stress 150GPA (TEM study)

Yielding under tensile stress

- Previous MD simulations with high strain rate: elastic up 30% (Yakoboson et al *)
- Experimentally feasible strain rate and Temperature



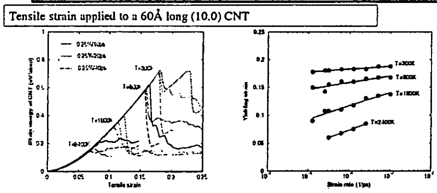
11.5% tensile strained (10,0) T=1600K

9% tensile strained (5,5) T=2400K

* Yakoboson et al, Comput. Mater. Sci. 8, 341 (1997)

Yielding: Strain-rate and Temperature dependence

Tensile strain applied to a 60Å long (10,0) CNT



- Yielding: strongly dependent on strain rate and Temperature
- Arrhenious Behavior: Linear dependent on temperature of the slope of yield strain vs strain rate

Transition State Theory

- Arrhenius formula: $t = \frac{1}{n_{site}} \frac{1}{\nu} e^{(E^0_v - VK\varepsilon)/k_B T}$

(Eyring's plastic doformation theory on polymers)

- Activation energy as a function of strain: $E_v = E^0_v - VK\varepsilon$
- Transition rate: $\frac{1}{\dot{\varepsilon}} = \frac{1}{n_{site}} \frac{1}{\dot{\varepsilon}_0} e^{\frac{E_v - VK\varepsilon}{k_B T}}$ $\Longrightarrow$ inversion

Yielding Strain under tension

$$\varepsilon_Y = \frac{\bar{E}_v}{VK} + \frac{k_B T}{VK} \ln\left(\frac{N\dot{\varepsilon}}{n_{site}\dot{\varepsilon}_0}\right)$$

$\dot{\varepsilon}$: Strain rate; : Constant related with vibrational frequency
: Force constant; : Activation volume; : Activation energy
: Number of process involving in yielding; n_{site} : Site available

Length effect: $\Delta\varepsilon_Y = -\frac{k_B T}{VK} \ln(n_{site}/n^0_{site})$

Temperature effect: $\left(\frac{\dot{\varepsilon} N}{\;}\right)^{T_1} = \left(\frac{\dot{\varepsilon} N}{\;}\right)^{T_2}$

Yielding at realistic conditions

- *Parameters obtained from fitting of MD simulations' data*

$\bar{E} = 3.6\text{eV};$

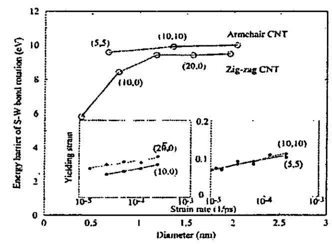
$\dot{\varepsilon}_0 = 8 \times 10^{-3}\ ps^{-1}$

- *Experimental feasible conditions*

length ~ 1μm; strain rate ~ 1/hour; T ~ 300K

$\Longrightarrow$ Yield strain: 9 ± 1 %

Energy barrier effect on yielding strain

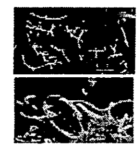


- C.Wei, D. Srivastava, and K. Cho, Phys. Rev. Lett. (submitted)
- D. Srivastava, C. Wei, and K. Cho, Appl. Mech. Review (2002)

Polymer-CNT composite

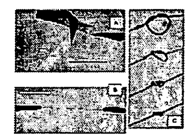
- Structural and thermal properties
- Load transfer and mechanical properties

SEM images of epoxy-CNT composite



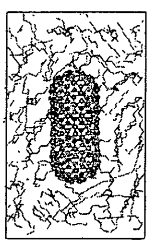
(L.S.Schadler et.al., Appl. Phys. Lett. V73 P3842, 1998)

SEM images of polymer (polyvinylacohol) ribbon contained CNT fibers & knotted CNT fibers



(B. Vigolo et.al., Science, V290 P1331, 2000)

MD simulations of Polymer-CNT



Polymer-CNT composite

Simulation Method

Classical MD: Tersoff-Brenner potentials and VDW interactions

System in simulation

Polyethylene & (10,0) CNT: (80 chains pf PE relaxed by Monte Carlo methods, Np=10; 20A long CNT 8% volume ratio)

Preparations:

Composites prepared at 300k; cooled down to 10K with rate 1K/1ps

composites change from liquid state through rubber state to glassy state

Thermal Characterization of Nanotubes and Polymer-Nanotube Composites

- Thermal conductivity of single-wall nanotubes
- Nanotube/polymer composites as high thermal expansion coefficient materials
- Thermal conductivity of nanotube/polymer composite

Thermal Conductivity of Nanotubes

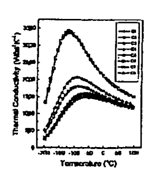
Thermal Conductivity of C based materials

CVD Diamond	1300 - 2000 W/mK ⁂
Graphite (basal plane)	1800 - 2000 W/mK ‡‡
CVD Silicon Carbide	259 - 272 W/mK ⁂
Aluminum Nitride (sintered)	174 - 182 W/mK ⁂
Copper	400 W/mK ⁂
Single walled Carbon nanotube Mat	[illegible] W/mK (as grown)
Single wall Carbon nanotube rope	1750 - 5800 W/mK #

based on the assumption that intrinsic and bulk thermal and electrical conductivity are related in the same way (J. Hone, et.al, Phys. Rev. B59, R2514, 1999)

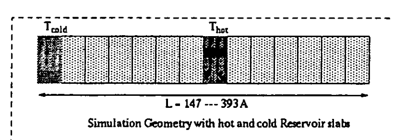
⁂ J E Graebner et.al, Diamond & Related Materials 7, 1589-1504, (1998).

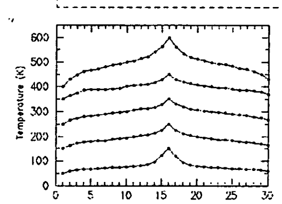
‡‡ B.T. Kelly, Physics of Graphite (Applied Science Publishers, London, 1981).



Temperature Dependence

Thermal Conductivity: Non-equilibrium MD

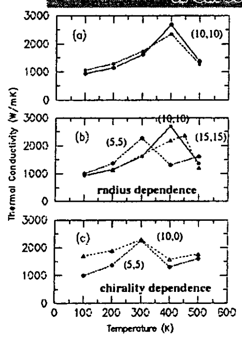




Temperature differential across nanotube

M. Osman and D. Srivastava, Nanotechnology, Vol. 12, 21 (2001)

Temperature Dependence of Thermal Conductivity of Carbon Nanotubes

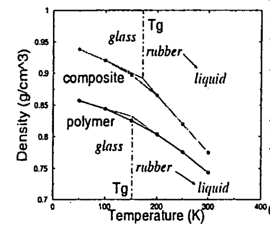


- Thermal peak position has a strong dependence on the radius of the tube and weak dependence on chirality
- Typical peak thermal conductivity is about 2000-3000 W/mK
- High thermal conductivity material with highly directional heat-flow and weak dependence on chirality

M. Osman and D. Srivastava, Nanotechnology, Vol. 12, 21 (2001)

High Thermal Expansion Coefficient Composite

Small system: L/D~2, Np=10



Results:

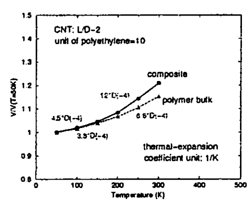
-Glass transition temperature Tg increased from 150K to 175K

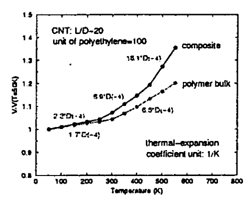
-Thermal expansion coefficients: (K^{-1})

	PE	PE-CNT	
$T<Tg$	3.8×10^{-4}	4.5×10^{-4}	↑18%
$T>Tg$	8.6×10^{-4}	12.0×10^{-4}	↑40%

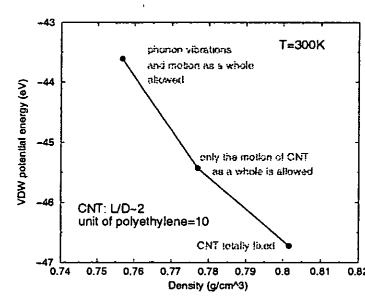
(Experimental value: $1.0\times10^{-4}\,K^{-1}$; T <Tg)

Thermal-expansion coefficients (large system)



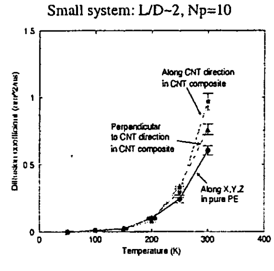


Increase in thermal-expansion of composite? Brownian motion and Surface Phonon Modes of Nanotube



Thermal Diffusion coefficients

Small system: L/D~2, Np=10



Diffusion coefficients of polymer with CNTs embedded

Diffusion coefficient increased, especially along CNT axis direction, indicating enhancement of thermal conductivity

* Experiments on ABS/CNT & RTV/CNT show large increase (Rick Berrerg's group at RICE)

* C. Wei, D. Srivastava, and K. Cho (submitted)

Modulus of Polymer-CNT composites

(Halpin-Tsai's formula)

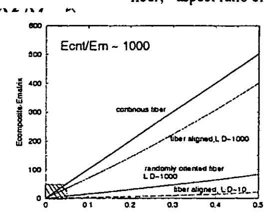
$$\frac{E_c}{E_m} = \frac{1+\xi\eta V_f}{1-\eta V_f}$$

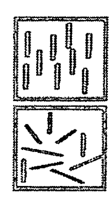
E_c, E_m, E_f :Modulus of composite, matrix and fiber

V_f : Volume ratio of fiber

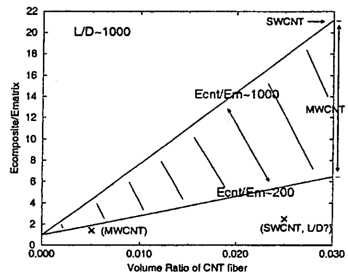
$$\eta = \frac{(M_f/M_m-1)}{(M_f/M_m+\xi)}$$

ξ: Dependent on geometry, packing of fiber; ~aspect ratio of fiber





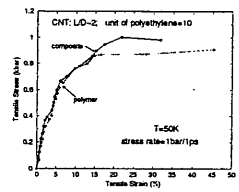
Experiments: Modulus of composites



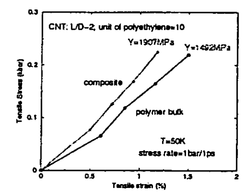
[*] D. Qian et al. App. Phys. Let., V76. P2868. 2000; R.Andrews et al. App. Phys.Let., V75. P1329.1999

Nanomechanics of Composite under Tensile Stress

Stress-Strain curve

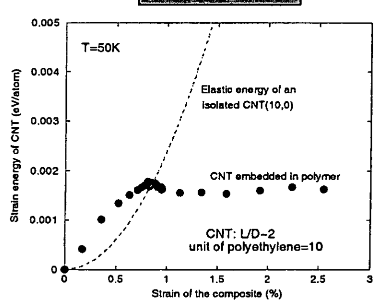


Young's Modulus



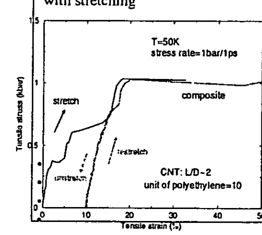
Nanomechanics of Composite under Tensile Stress

Strain energy of CNT



Loading sequence

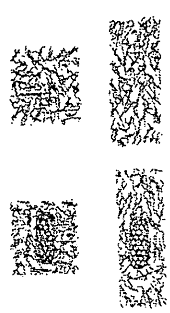
Work hardening of composite with stretching



TEM images of alignment of CNTs in a polymer matrix by stretching

(L. Jin et.al., Appl.Phys. Lett., V73 P1197. 1998)

Polymer-CNT composite: Effect of Stretching

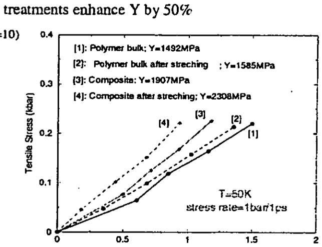


Young's Modulus

-Young's modulus of CNT composites 30% higher than polymer matrix

-Stretching treatments enhance Y by 50%

(L/D~2. Np=10)



Comments

- Nanomechanics of individual nanotubes explained experimental observations, and revealed *novel anisotropic strain release in BN* nanotubes
- Realistic strain-rate, temperature and length dependent deformation of nanotubes under tensile strain id developed
- Polymer-nanotube composite is a high thermal expansion coefficient and diffusion material above glass transition temperature
- Young's modulus increases by upto 30% for low strain values, this can be further increased by stretching-unstretching cycling of composite
- Multiple-site chemical bonding favors load transfer